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Supplementary Material Available: Tables of bond distances and angles, least-squares planes, torsional angles, and general displacement parameter expressions for (C$_6$H$_5$)$_2$Mo(O)$_2$(bpy) and (C$_6$H$_5$)$_2$W(O)$_2$(bpy) (28 pages); listings of observed and calculated structure factors (41 pages). Ordering information is given on any current masthead page.

Multidentate Lewis Acids. Complex of a Macrocyclic Host with a Bidentate Guest

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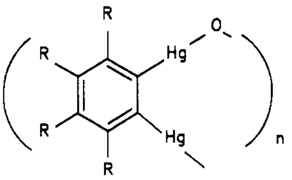
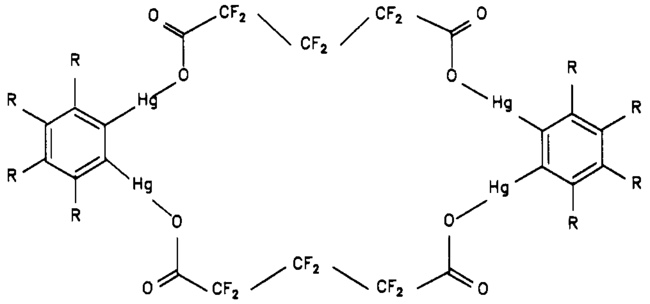
Summary: Neutralization of the mercuric oxide **1b** with hexafluoroglutaric acid in 1,2-dimethoxyethane (DME) produces the 1:4 DME adduct of macrocyclic tetradentate Lewis acid **2b** in 76% yield. An X-ray crystallographic study revealed that the macrocyclic host is approximately planar and that each 1,2-phenylenedimercury unit is associated with two molecules of DME, one above the plane and the other below. One oxygen atom from each molecule of DME bridges the two mercury atoms, and the other oxygen interacts with a single mercury. The resulting adduct is the first structurally characterized complex in which a basic guest and a multidentate Lewis acidic host share more than two bonds.

Multidentate Lewis acids with cleverly oriented electrophilic sites promise to be useful for the recognition, binding, transport, and chemical activation of complementary basic substrates.[1,2] We have shown that macrocyclic Lewis acidic hosts can be prepared by the simple expedient of neutralizing suitable organometallic oxides with perfluoro dicarboxylic acids.[1h,3] For example, treatment of (μ-1,2-phenylene)(μ-oxo)dimercury (**1a**) with an equimolar amount of hexafluoroglutaric acid in tetrahydrofuran (THF) produces a complex of the tetradentate macrocycle **2a** in high yield.[1h] In this article, we describe an extremely convenient synthesis of the octamethyl derivative **2b**, and we show how this multidentate host binds a bidentate guest.[2]



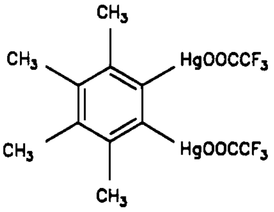
1a (R = H)

1b (R = CH$_3$)



2a (R = H)

2b (R = CH$_3$)



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Direct bismercuration of 1,2,3,4-tetramethylbenzene (Hg(OOCCF$_3$)$_2$, CF$_3$COOH, 25 °C)[4] produced the bis(trifluoroacetate) **3** in 75% yield. Treatment of compound **3** with aqueous NaOH (0.16 N, reflux) then gave a quantitative yield of the corresponding oligomeric oxide **1b**. Neutralization of oxide **1b** with an equimolar amount of hexafluoroglutaric acid in 1,2-dimethoxyethane (DME) provided a 76% yield of crystals of a complex of macrocycle **2b** with DME. This synthesis is noteworthy because it produces a macrocyclic multidentate Lewis acid in three efficient steps from an inexpensive precursor.

Elemental analysis and ^{1}H NMR spectroscopy demonstrated that the complex contains one molecule of DME per atom of mercury. An X-ray crystallographic study revealed that the adduct has the novel structure shown in Figure 1. The macrocyclic host is approximately planar and binds two molecules of DME above the plane and two below. The two bidentate 1,2-phenylenedimercury units from which the macrocycle is built operate independently, and each binds two molecules of DME, one above the plane and the other below. One oxygen atom from each molecule of DME bridges the two mercury atoms of a 1,2-phenylenedimercury unit, and the other oxygen interacts with a single mercury. The resulting adduct is the first structurally characterized complex in which a basic guest and a multidentate Lewis acidic host share more than two bonds.

Selected interatomic distances, bond angles, and torsion angles are listed in Table I, and atomic coordinates and isotropic thermal parameters are provided in Table II. These data establish that the macrocyclic hosts in the 1:2 THF complex of hexafluoroglutarate **2a** and the 1:4 DME complex of hexafluoroglutarate **2b** have very similar

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Table I. Selected Interatomic Distances, Bond Angles, and Torsion Angles in the 1:4 Complex of Macrocyclic Mercuric Hexafluoroglutarate 2b with DME

Distances (Å)			
Hg(1)-C(1)	2.046 (8)	Hg(2)-C(2)	2.057 (8)
Hg(1)-O(111)	2.094 (6)	Hg(2)-O(151)[a]	2.092 (6)
Hg(1)-O(112)	3.014 (7)	Hg(2)-O(152)[a]	3.042 (7)
Hg(1)-O(32)	2.850 (7)	Hg(2)-O(35)	3.006 (5)
Hg(1)-O(35)	2.776 (6)	Hg(2)-O(42)	2.987 (7)
Hg(1)-O(45)	3.052 (6)	Hg(2)-O(45)	2.866 (6)
Hg(1)-Hg(2)	3.4442 (5)	Hg(1)-Hg(2)[a]	9.0998 (5)
Bond Angles (deg)			
C(1)-Hg(1)-O(111)	178.5 (3)	C(2)-Hg(2)-O(151)[a]	176.5 (3)
C(1)-Hg(1)-O(32)	94.6 (3)	C(2)-Hg(2)-O(35)	95.2 (2)
C(1)-Hg(1)-O(35)	101.2 (2)	C(2)-Hg(2)-O(42)	89.5 (3)
C(1)-Hg(1)-O(45)	93.9 (2)	C(2)-Hg(2)-O(45)	98.6 (2)
Hg(1)-O(111)-C(11)	113.8 (5)	Hg(2)-O(151)[a]-C(15)[a]	113.0 (5)
O(111)-Hg(1)-O(112)	47.4 (2)	O(151)[a]-Hg(2)-O(152)[a]	48.0 (2)
O(111)-Hg(1)-O(32)	84.1 (2)	O(151)[a]-Hg(2)-O(35)	87.0 (2)
O(111)-Hg(1)-O(35)	78.7 (2)	O(151)[a]-Hg(2)-O(42)	90.5 (2)
O(111)-Hg(1)-O(45)	87.6 (2)	O(151)[a]-Hg(2)-O(45)	84.5 (2)
Torsion Angles (deg)			
C(31)-O(32)-C(33)-C(34)	179.5 (9)		
O(32)-C(33)-C(34)-O(35)	62.3 (10)		
C(33)-C(34)-O(35)-C(36)	76.6 (9)		
C(41)-O(42)-C(43A)-C(44)	-177.5 (11)		
O(42)-C(43A)-C(44)-O(45)	-64.1 (15)		
C(43A)-C(44)-O(45)-C(46)	163.4 (11)		
O(111)-C(11)-C(12)-C(13)	56.4 (10)		
C(11)-C(12)-C(13)-C(14)	167.2 (7)		
C(12)-C(13)-C(14)-C(15)	168.6 (7)		
C(13)-C(14)-C(15)-O(151)	-78.9 (9)		

[a] Symmetry transformation: $1 - x, 2 - y, 2 - z$.

structures. Specifically, the average Hg–C distances (2.14 (6) and 2.052 (8) Å), Hg–OCO distances (2.10 (4) and 2.093 (6) Å), C–Hg–OCO angles (174 (2) and 177.5 (3)°), and distances from Hg to the bridging oxygen of the guest (2.85 (4) and 2.925 (6) Å) differ by less than twice the estimated standard deviations. In both structures, mercury shows a marked preference for forming two strong collinear primary bonds, and it retains appreciable acidity in the plane perpendicular to these primary bonds, allowing secondary coordinative interactions to take place. Both macrocycles incorporate almost fully extended hexafluoroglutarate chains with $CO-CF_2-CF_2-CF_2$ dihedral angles between 158 and 168°. The $O-CO-CF_2-CF_2$ dihedral angles vary significantly, presumably in response to the guests, but both macrocycles nevertheless create central holes that are approximately 3.5 Å wide and 9.0 Å long measured from mercury to mercury.

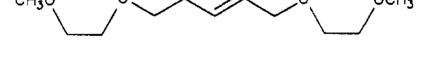
In principle, neutralization of oxides **1a** and **1b** with dicarboxylic acids could produce either linear polymers or macrocyclic oligomers. The observed macrocyclization may simply reflect fortuitously favorable kinetics of formation or crystallization, but the close structural similarity of products **2a** and **2b** suggests that macrocyclization may have a deeper explanation. Both macrocycles incorporate 1,2-phenylenedimercury and hexafluoroglutarate in conformations that do not introduce significant amounts of additional strain. As a result, the enthalpies of linear polymerization and the observed macrocyclization must be very similar, while the entropy of polymerization is necessarily more negative. We conclude that macrocyclization may be attractive thermodynamically as well as kinetically.

Table II. Atomic Coordinates (×10⁴, Hg × 10⁵) and Isotropic Thermal Parameters (×10³ Å²) for the 1:4 Complex of Macrocyclic Mercuric Hexafluoroglutarate 2b with DME

atom	*x*	*y*	*z*	U_{eq}
Hg(1)	45156 (4)	78926 (3)	69184 (2)	37
Hg(2)	22973 (4)	61363 (3)	81369 (2)	34
F(121)	6990 (6)	11899 (4)	7355 (4)	58
F(122)	9139 (5)	11268 (4)	7424 (4)	54
F(131)	8557 (6)	10418 (4)	9109 (4)	55
F(132)	6673 (5)	11417 (5)	9061 (4)	55
F(141)	8715 (6)	13462 (4)	8768 (4)	53
F(142)	10471 (5)	12386 (5)	9118 (4)	62
O(32)	2552 (7)	9361 (6)	6139 (5)	60
O(35)	2509 (6)	8795 (5)	8008 (4)	40
O(42)	4213 (8)	4289 (6)	8573 (6)	75
O(45)	5425 (7)	6861 (6)	8693 (5)	57
O(111)	5740 (6)	9556 (5)	7570 (5)	53
O(112)	7565 (7)	9167 (6)	6757 (5)	65
O(151)	7852 (6)	13401 (5)	10444 (4)	45
O(152)	9935 (7)	12623 (6)	10854 (5)	64
C(1)	3296 (9)	6289 (7)	6255 (6)	31
C(2)	2329 (8)	5604 (7)	6736 (6)	29
C(3)	1454 (9)	4537 (7)	6279 (6)	35
C(4)	1537 (9)	4148 (7)	5339 (6)	38
C(5)	2450 (9)	4837 (7)	4850 (6)	39
C(6)	3322 (9)	5927 (7)	5296 (6)	36
C(7)	382 (11)	3805 (8)	6790 (7)	55
C(8)	607 (11)	2963 (8)	4850 (7)	61
C(9)	2511 (12)	4416 (9)	3821 (7)	67
C(10)	4303 (11)	6708 (8)	4754 (7)	52
C(11)	6990 (9)	9792 (7)	7298 (6)	37
C(12)	7776 (9)	11088 (7)	7717 (6)	37
C(13)	8002 (9)	11374 (7)	8777 (6)	36
C(14)	9056 (9)	12532 (7)	9240 (7)	41
C(15)	8979 (9)	12880 (8)	10297 (6)	40
C(31)	2876 (17)	10124 (13)	5477 (10)	116
C(33)	1516 (11)	9752 (8)	6688 (7)	53
C(34)	1230 (10)	8863 (8)	7376 (7)	51
C(36)	2865 (12)	9803 (9)	8739 (7)	59
C(41)	3776 (15)	3171 (11)	7993 (10)	88
C(43A)[a]	5571 (16)	4733 (13)	8202 (13)	74
C(43B)[a]	5568 (39)	4985 (33)	9155 (22)	62
C(44)	6249 (12)	5860 (10)	8726 (10)	83
C(46)	5971 (13)	7829 (10)	9418 (8)	78

[a] C(43A) occupancy 0.70; C(43B) occupancy 0.30.

Spectroscopic evidence has suggested that DME adopts a t–g–t conformation in its 1:1 complex with $HgCl_2$.[5] Two of the four molecules of DME bound by macrocyclic host **2b** show a similar preference, while the other two adopt a t–g–g conformation. Complexation could not be studied in solution because DME is displaced by solvents in which its adduct with host **2b** is soluble. One of the most intriguing features of the structure is the use of space above and below the center of the macrocycle by the guests. In both regions, methyl groups from different DME molecules face each other across the ring. This orientation suggests that a geometrically suitable tetradentate ether could span the entire surface of macrocyclic hosts **2a** or **2b** and make simultaneous contact with all four atoms of mercury. Tight binding of octadentate guest **4** is an even more interesting



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possibility, since perpendicular inclusion of its aromatic core in the central hole of macrocyclic hosts **2a** and **2b**

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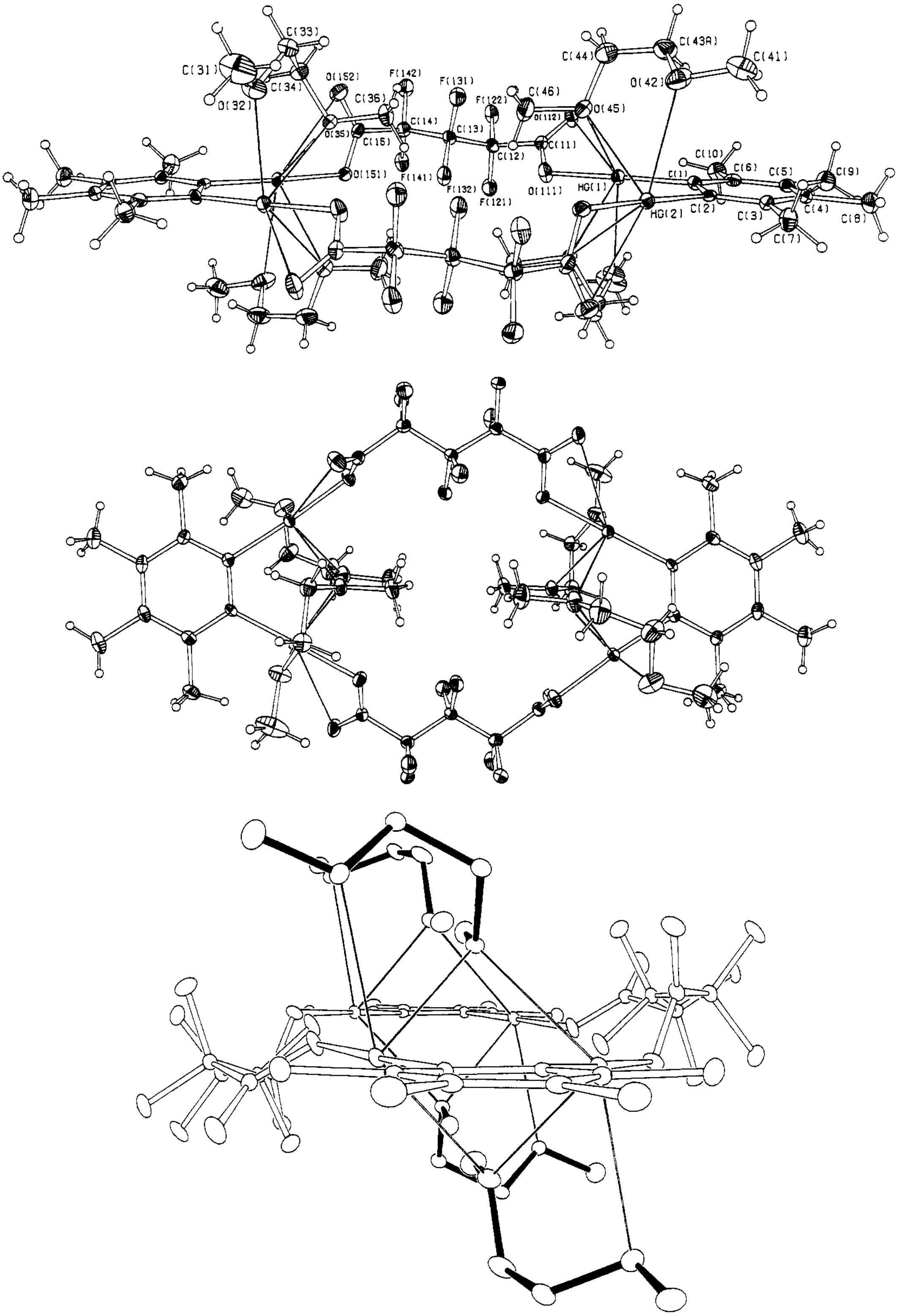

Figure 1. ORTEP drawings of three views of the 1:4 complex of macrocyclic mercuric hexafluoroglutarate **2b** with DME. The non-hydrogen atoms are represented by ellipsoids corresponding to 50% probability. In the upper two views, hydrogens are shown as spheres of arbitrary size. In the bottom view, the hydrogens are omitted for simplicity.

should allow the basic bidentate arms of the guest to have simultaneous contact with all four atoms of mercury on both surfaces of the host. The detailed structural information available for adducts of multidentate Lewis acids **2a** and **2b** now lets us accept the challenge of building related macrocyclic and macrobicyclic hosts by design.

Experimental Section

Infrared (IR) spectra were recorded on a Perkin-Elmer Model 783 spectrometer. Varian VXR-300 and Bruker WH-90 spectrometers were used to obtain ^{1}H nuclear magnetic resonance (NMR) spectra. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane. The Varian instrument was used to record ^{199}Hg NMR spectra at 53.6 MHz. Chemical shifts are reported in parts per million relative to dimethylmercury. Galbraith Laboratories, Knoxville, TN, performed all elemental analyses. Melting points were recorded on a Thomas-Hoover capillary apparatus and are not corrected. DME (1,2-dimethoxyethane) was dried by distillation from the sodium ketyl of benzophenone, and hexafluoroglutaric acid was purified by distillation. All other reagents were commercial products of the highest purity available.

Bis(trifluoroacetato-*O*)(3,4,5,6-tetramethyl-1,2-phenylene)dimercury (3). Mercuric trifluoroacetate (1.36 g, 3.19 mmol) was added to a solution of 1,2,3,4-tetramethylbenzene (0.211 g, 1.57 mmol) in trifluoroacetic acid (8 mL). The mixture was stirred at 25 °C for 15 min and then poured into water (40 mL). The resulting precipitate was separated by centrifugation, washed thoroughly with water, and dried in vacuo. Sublimation (10^{-5} Torr, 100 °C) removed the product of monomercuration[6] and left a residue of the bis(trifluoroacetate) **3** (0.898 g, 1.18 mmol, 75.2%). Recrystallization from chloroform/acetonitrile provided colorless crystals of an analytically pure sample: mp >300 °C; IR (KBr) 1680, 1445, 1210, 1160 cm^{-1}; ^{1}H NMR (90 MHz, DMSO-d_6) δ 2.17 (s, 6 H), 2.38 (s, 6 H); ^{199}Hg NMR (53.6 MHz, DMSO-d_6, 0.1 M) δ −1493. Anal. Calcd for $C_{14}H_{12}F_6Hg_2O_4$: C, 22.14; H, 1.60. Found: C, 22.10; H, 1.56.

(μ-3,4,5,6-Tetramethyl-1,2-phenylene)(μ-oxo)dimercury (1b). Bis(trifluoroacetate) **3** (410 mg, 0.54 mmol) was heated at reflux for 20 min in aqueous NaOH (0.16 N, 35 mL). The mixture was cooled, and the suspended solid was separated by centrifugation, washed thoroughly with water, and dried in vacuo to give the oligomeric oxide **1b** as a white powder (300 mg, 0.54 mmol, 100%): mp >300 °C; IR (KBr) 2950 (br), 1470, 645, 460 cm^{-1}. This product was used for the following reaction without further purification.

1:4 DME Adduct of the Macrocyclic Mercuric Hexafluoroglutarate 2b. Oxide **1b** (40.9 mg, 74.4 μmol) was added at 25 °C under dry N_2 to a solution of hexafluoroglutaric acid (19.0 mg, 79.1 μmol) in DME (30 mL). The mixture was stirred for 15 min; then the flask was opened to the atmosphere, and the solvent was allowed to evaporate slowly. This yielded colorless crystals of the 1:4 DME adduct of macrocyclic mercuric hexafluoroglutarate **2b**, which were removed by filtration and dried in vacuo (54.1 mg, 28.4 μmol, 76.3%): mp 236–237 °C dec; IR (KBr) 1700, 1380, 1340, 1250, 1145 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 2.06 (s, 12 H), 2.26 (s, 12 H), 3.22 (s, 24 H), 3.41 (s, 16 H); ^{199}Hg NMR (53.6 MHz, DMSO-d_6, 0.01 M) δ −1474. Anal. Calcd for $C_{46}H_{64}F_{12}Hg_4O_{16}$: C, 29.02; H, 3.40. Found: C, 28.79; H, 3.31.

Crystallographic Data for the 1:4 DME Adduct of Host 2b. The crystal selected for analysis had the dimensions 0.16 × 0.22 × 0.36 mm. It proved to belong to the triclinic space group $P\bar{1}$, with a = 9.141 (3) Å, b = 11.203 (4) Å, c = 14.563 (11) Å, α = 97.34 (4)°, β = 96.70 (4)°, γ = 97.45 (3)°, V = 1453.1 Å^3, Z = 1, and D_{calcd} = 2.175 g cm^{-3}.

Crystallographic Measurements and Structure Resolution. An Enraf-Nonius CAD-4 diffractometer was used to collect a set of intensity data according to a procedure described elsewhere.[7] Seven standard reflections checked every 1 h showed random fluctuations of less than ±2.1% about their respective means. A set of 7586 Mo K$\bar{\alpha}$ reflections ($2\theta \leq 45°$) was collected at 220 K. Of these, 2963 ($I > 3\sigma(I)$) were retained for structure resolution and refinement after averaging to the Laue $\bar{1}$ symmetry. These measurements were corrected for the Lorentz effect, polarization, and absorption (Gaussian integration technique) before averaging. The structure was solved by using direct methods (EEES) and difference-Fourier calculations (SHELX), and it was refined on $|F_o|$ by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at idealized positions (C–H = 0.95 Å, B_{iso} = 7 Å^2 (phenyl) and 8 Å^2 (others)). Disorder was introduced at C(43) to account for its large anisotropic behavior. The occupancy was initially refined and then fixed at 0.70/0.30. Refinement converged to R = 0.025, R_w = 0.027, and goodness-of-fit ratio S = 1.67 for 363 parameters refined. The final ΔF map was essentially featureless, with a general background below ±0.18 e Å^{-3} and 15 peaks of 0.20–0.54 e Å^{-3} within 1.15 Å from Hg. The scattering curves for the non-hydrogen atoms[8] and the hydrogen atoms[9] were taken from standard sources. The contributions of Hg to anomalous dispersion were included.[10]

Selected interatomic distances, bond angles, and torsion angles are listed in Table I, and atomic coordinates and isotropic thermal parameters are provided in Table II. Tables of hydrogen atom coordinates, anisotropic thermal parameters, interatomic distances, bond angles, and structure factors are included as supplementary material.

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Registry No. **1b**, 125611-04-3; **2b**, 125640-18-8; **3**, 125611-05-4; $Hg(OOCCF_3)_2$, 13257-51-7; 1,2,3,4-tetramethylbenzene, 488-23-3; hexafluoroglutaric acid, 376-73-8.

Supplementary Material Available: Tables of hydrogen atom coordinates, anisotropic thermal parameters, and interatomic distances and bond angles for the 1:4 DME complex of macrocyclic mercuric hexafluoroglutarate **2b** (8 pages); a table of structure factors (14 pages). Ordering information is given on any current masthead page.

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Rotational Behavior of *exo*-[1,1,3-Tris(trimethylsilyl)allyl]lithium

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Summary: The title compound, **3**, has been generated by metalation of (*E*)-1,3,3-tris(trimethylsilyl)-1-propene with butyllithium[^{6}Li] in pentane–TMEDA at room temperature. NMR establishes the exo structure of **3** under all conditions used. Compound **3** in THF with 1 equiv of TMEDA exhibits a barrier to rotation about the C_1C_2 bond of $\Delta H^\ddagger$ = 17 kcal and $\Delta S^\ddagger$ is +25 eu.

Allyllithium and substituted versions thereof have been the subject of extensive investigations of their chemistry[1] by X-ray crystallography,[2] with NMR,[3] and by calculation.[4]

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